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(71) Applicant *(for all designated States except US)*: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : HARDY, Frederick, Edward [GB/GB]; 8 Woodend, Darras Hall, Newcastle upon Tyne NE20 9ES (GB). INGRAM, Barry, Thomas [GB/GB]; 47 Western Way, Whitley Bay, Tyne & Wear NE 26 1EJ (GB).

(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45202 (US).

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(54) Title: BLEACHING COMPOSITIONS

(57) Abstract

A bleaching composition useful for the bleaching of stained articles, comprises (a) a urea clathrate of a diacyl or tetraacyl peroxide, e.g. dinonanoyl peroxide, dioctanoyl peroxide or diperoxyazelaic diacetate. The composition may also comprise (b) a compound capable of yielding hydrogen peroxide in an aqueous medium, e.g sodium perbonate. The composition, which can be effective against carotenoid stains, is generally in granular form and may be formulated as a laundry detergent composition that also comprises (c) an anionic, nonionic, cationic, ampholytic or zwitterionic detersive surfactant and, optionally, (d) a detergent builder and/or (e) a bleach activator.

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BLEACHING COMPOSITIONS

Field of invention

The present invention relates to compositions that are useful in the bleaching of stains from soiled articles, including and of particular use in the bleaching of carotenoid-containing stains. In one aspect, the invention relates to such compositions that are in the form of detergent compositions comprising one or more detersive surfactants.

Background to the invention

It is well known to incorporate into a detergent composition an inorganic compound that is capable of yielding hyrdogen peroxide in an aqueous medium, a common example of such a compound being sodium perbonate. The resultant compositions are effective in the removal of certain hydrophilic stains, for example those due to tea, wine or fruit juice, but, on its own, the bleaching agent has to be used at a temperature of at least 60°C. In order to render such compositions effective at lower temperatures, for example 30-40°C, it has been proposed to add an activator, such as tetraacetylethylenediamine (TAED), such activators being thought to react in solution with the perbonate and thereby yield peroxyacetic acid. In order to bleach such hydrophobic stains as those due to grass, motor oil, paprika and the "dinginess" associated with repeated laundering of fabrics, it has been proposed to add monanoyloxybenzene sulfonate (NOBS), which is an aqueous medium in the presence of perbonate is thought to produce peroxynonanoic acid. However, there are a number of common soils that give rise to hydrophobic stains that are resistant to the NOBS/perbonate system, such stains being due to carotenoid chromophores, e.g. ß-carotene, lycopene, zeaxanthin or capsanthin. Typical soils giving rise to such stains include carrot and tomato, and baby-

foods and sauces containing or or both of these, as well as various tropical fruits and saffron.

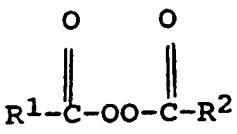
One proposal for the removing of a wide range of stains, including such hyrophobic stains as those caused by tomato sauce, is described in EP-A-0,337,535, which recommends the use of a bleaching composition that comprises (i) a peroxygen bleaching compound capable of yielding hydrogen peroxide in an aqueous medium, preferably sodium perbonate monohydrate or tetrahydrate, and (ii) a bleach precursor having the general formula R-CO-L wherein R is one of certain aromatic or substituted aromatic radicals, e.g. a (C_1-C_6-alkyl)phenyl or unsubstituted phenyl group, and wherein L is a leaving group, preferably a 4-sulfophenyl group, the molar ratio of hydrogen peroxide to precursor being within the range of from 0.1 to 2. However, the pH of the aqueous medium appears to be critical to the bleaching performance of these compositions, it being stated in that European application (page 4, lines 20-22) that the pH must fall between 8.5 and 9.4.

EP-A-0, 106,584 discloses bleaching compositions that are described as being effective not only against a very wide class of stains but also over a very wide range of pH of the bleaching solution. Specifically, these compositions comprise (a) a halogenated peroxybenzoic acid or a salt thereof, e.g. p-chloro- (or p-fluoro-) peroxybenzoic acid or its mangesium salt, and (b) a bleach activator having the general formula R-CO-L, wherein R is selected from certain alkyl, alkylene, cycloalkyl, cycloalkylene, aryl, aromatic heterocyclic or polyarylene groups or groups in which two or more aryl or arylene substituents are covalently attached. Also disclosed are bleaching compositions containing (a) a peroxycarboxylic acid or salt thereof and (b) a bleach activator having the general formula R-CO-L wherein R is a C_5-C_{17} alkyl group. In both cases, L is a leaving group wherein the conjugate acid of the anion formed on L has a pk_a of from 4 to 13 and the molar ratio of each peroxycarboxyl group of (a) to each

carbonyl group of (b) that can potentially generate a diacyl peroxide compound is from 10 to 0.05. It is surmissed in EP-A-0, 106,584 (page 5, lines 1 - 13) that the bleaching performance of these compositions is due to the reaction of the perxycarboxylic acid with the bleach activator within an aqueous medium to from a diacyl peroxide compound.

Summary of invention

The present invention relates to the use in bleaching compositions of urea clathrates of peroxide compounds, which peroxide compounds are selected from (1) diacyl peroxides of the general formula:

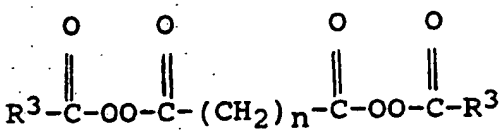


in which

R^1 represents a C_6-C_{18} alkyl group containing a linear chain of at least 5 carbon atoms and optionally containing one or more substituents (e.g. $-N^+(CH_3)_3$, -COOH or -CN) and/or one or more interrupting moieties (e.g. -CONH- or -CH=CH-) interpolated between adjacent carbon atoms of the alkyl radical, and

R^2 represents an aliphatic or aromatic group compatible with a peroxide moiety, such that R^1 and R^2 together contain a total of 8 to 30 carbon atoms,

and (2) tetraacyl peroxides of the general formula :



in which

R^3 represents a C_1-C_9 alkyl group, and n represents an integer from 2 to 12 inclusive.

The bleaching compositions comprising the urea clathrates as defined above may find use in essentially any bleaching process. The bleaching compositions, for example are useful in the bleaching of cellulosic fibrous material. The term cellulosic fibrous material as used herein has reference to wood, cotton, linen, jute and other materials of a cellulosic nature, and also includes individual fibres, for example wood pulp or cotton fibre, as well as yarns, tows, webs, fabrics (woven or non-woven) and other aggregates of such fibres. The bleaching compositions of the invention are also useful in the bleaching of synethic textiles including polyamides, vicose, rayon, and polyesters.

The bleaching compositions are also useful as components of detergent compositions. These detergent compositions may be used in essentially any washing laundering or cleaning processes in which bleaching is required. Thus, the detergent compositions may be used in home or industrial laundering or automatic dishwashing processes, and in any process involving the cleaning of hard surfaces such at bottle washing, dairy cleaning and kitchen and bathroom cleaning processes.

In one of its aspects, the invention provides a detergent composition useful in the bleaching of stains from soiled articles which detergent composition comprises (A) an urea clathrate as defined above and at least one component selected from (B) a source of hydrogen peroxide selected from nonionic, anionic, cationic, ampholytic and zwitterionic detersive surfactants. Compositions to be used merely for bleaching may omit component (C) whereas compositions intended for use in the laundering of bleach-sensitive coloured fabrics (so-called "colour-care" laundry compositions) may omit component (B).

In a preferred aspect of the invention there is provided a composition in the form of a detergent composition containing both of components (B) and (C) : optional,

ingredients for such detergent compositions include (D) a detergent builder compound and (E) a bleach activator.

Description of exemplary embodiments

The diacyl peroxides of the genral formula (1) are known compounds, of which a number are sold commercially as free-radical polymerisation initiators and the like, or can be prepared by methods known in principle. Thus, for example, it is stated in the Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 9, at page 815, that diacyl peroxides can be prepared by treating an acid chloride or anhydride with sodium peroxide or hydrogen perodxide in the presence of a base. Methods for the preparation of diacyl peroxides are also described by L.S. Silbert and D. Swern, J. Amer. Chem. Soc., 81 (1959), 2364. The diacyl peroxides of the general formula (1) include those in which R^2 is selected from optionally substituted and/or interrupted C_1-C_{18} alkyl radicals, phenyl and benzyl.

Examples of such peroxides are :

C_9H_{19} -NHCO-$(CH_2)_4$-CO-OO-CO-CH_3
C_9H_{19} -NHCO-$(CH_2)_4$-CO-OO-CO-C_8H_{17} and
C_9C_{19} -NHCO-$(CH_2)_4$-CO-OO-CO-$(CH_2)_2$-CO_2H

Thus, R^2 may be selected from the radicals specified for R^1, that is to say C_6-C_{18} alkyl radicals containing a linear chain of at least 5 carbon atoms and optionally containing one or more substituents and/or one or more interrupting moieties interpolated between adjacent carbon atoms of the alkyl radical. Usually, however, the said alkyl radicals R^1 and R^2 will be unsubstituted and uninterrupted and hence will usually have a linear chain of at least $-(CH_2)_5-$, preferably at least $-(CH_2)_9-$, straight-chain alkyl radicals being preferred. Diacyl peroxides of the formula (1) in which R^1 and R^2 are identical will commonly be used, particularly preferred compounds being

dinonanoyl peroxide (also known as dipelargonyl peroxide), of the formula n-$H_{17}C_8$-CO-OO-CO-C_8H_{17}-n,

and dioctanlyl peroxide, which is commercially available as N.S. Tsvetkov et *al*, Vysokomol. Soyed., A14, No. 9 (1972), 2072-2077. Alternatively, tetraacyl peroxides may be prepared from a diperoxy dicarboxylic acid and an acyl chloride (e.g. from diperoxyadipic or diperoxyazelaic acid and acetyl chloride) in the presence of pyridine, as described by L.S. Silbert and D. Swern, J. Amer. Chem. Soc. 81 (1959), 2364. In the tetraaceytl peroxides of the formula (2) the R^3 radicals will usually be identical, although they can be different. It is preferred that each R^3 represents n-C_8H_{17}-and n is 10.

The diacyl and tetraacyl peroxides are intrisically unstable above their melting points and are liable to self-accelerating thermal (and catalytic) decomposition ; they should generally be handled with great caution in view of their flammability and their tendency to decompose explosively when heated or subjected to shock or friction. The peroxides commonly have a 10-hour half-life temperature of less than 100°C, a number of peroxides that are particularly useful in the present invention having 10-hour half-life temperatures of only 55-65°C. It has been found, however, that the urea clathrates of the peroxides may show much greater stability : for example, whereas dinonanoyl peroxide melts, and hence becomes extremely unstable, at about 20°C, a test using differential scanning calorimetry indicated that an urea clathrate of dinonanoyl peroxide was stable to at least 125°C, which is not far short of the melting point (133°C) of urea itself.

The urea clathrates (also known as urea inclusion compounds, urea complexes or urea adducts) of diethyl peroxides and tetraacyl peroxides are known or can be prepared by methods known in principle, for example by mixing a solution containing the peroxide in methanol or propan-2-ol with a solution of urea in methanol, the peoxide/urea ration corresponding to the expected

stoichiometry of the clathrate or to an excess of the peroxide, as described by K.D.M. Harris and J.M. Thomas, J. Chem. Soc. Faraday Trans., 1990, 86 (17), 2985-2996. urea clathrates of tetraacyl peroxides are described by L. Heslinga and W. Schwaiger, Recueil, 85 (1986), 75-85, which authors disclose that such a clathrate may be formed by mixing te diperoxy acid, e.g. diperoxyadipic, diperoxyazelaic or diperoxysuccinic acid, with the calculated amounts of urea and acetic anhydride. As a general guide, from 2.5 to 3.5, typically about 3, parts by weight of urea will be required for the clathration of one part of the weight of the peroxide.

The urea clathrate will be incorporated in the bleaching or detergent compositions of this invention at a level corresponding to usually at least 0.1 percent, preferably at least 0.25 percent and more preferably at least 1 percent and usually up to 20 percent, preferably up to 10 percent and more preferably up to 5 percent by weight of diacyl or tetraacyl peroxide, based on the total composition.

When employed in bleaching, cleaning, washing or laundering processes, the bleaching detergent compositions of the invention will be used in an aqueous solution such that the level of diacycl or tetraacyl peroxide is preferably from 0.001% to 0.5% by weight, more preferably from 0.005% to 0.02% by weight of the solution.

The source of hydrogen peroxide used as component (B) can be selected from a wide variety of compounds that are capable of yielding hydrogen peroxide in an aqueous medium. Inorganic compounds serving as sources of hydrogen peroxide and which can be used as component (B) in the present compositions are well known in the art and include such persalts as perborates, percarbonates, perphosphates and persulfonates. The alkali metal persalts are preferred, especially the sodium persalts. Sodium perborate, typically as the monohydrate or tetrahydrate, is preferably used. However, a suitable organic compound may be used,

for example a perhydrate of urea or of an organic acid salt.

The compound (B), if used, will be present in the composition in an amount of usually at least 0.5 percent, preferably at least 0.1 percent and more preferably at least 0.5 percent and usually up to 60 percent, preferably up to 30 percent and more preferably up to 20 percent, by weight of the total composition.

The weight ratio of component (A) to component (B) may be varied widely. In general, a lower level of H_2O_2-source, especially in the presence of one of the more hydrophilic acyl peroxides, will favour carotenoid bleaching, whereas a higher level will promote peracid formation and hence will disfavour carotenoid bleaching.

The detersive surfactant (C) will typically be used in an amount of from 0 to 50, preferably 1 to 30 and more preferably 5 to 20 percent by weight.

The compositions of the present invention will normally be in granular form, which expression herein includes any solid particulate form that is appropriate for bleaching, detergent or other cleaning compositions. The compositions of this invention may be formulated as simple bleaching compositions, as colour-care detergent compositions that contain no source of H_2O_2, or even as dishwashing compositions or hard-surface, toilet or other household cleaners. In certain preferred embodients, however, they are formulated as detergent compositions (typically, general-purpose or heavy duty compositions) that contain not only the above-discussed components (A) and (B) but also (C) a detersive surfactant and, optionally, (D) a detergent builder and/or (E) a bleach activator. The composition may also comprise any other component conventional in the art, for example an enzyme, a polymeric soil-release agent, a chelating agent, a clay soil removal/anit-redeposition agent, a polymeric dispersing agent, a brightener, a suds suppressor, a pH-buffering agent, a dye or a pigment.

It will be understood that any of the above mentioned components, whether essential or optional, may be constituted, if desired, by a mixture of two or more compounds of the appropriate description.

Examples of various optional components that come into consideration for inclusion in the present compositions are as follows.

Nonionic Surfactants

The detergent compositions of this invention may contain a nonionic surfactant.

Suitable nonionic surfactants include the polyethylene oxide condensates of alkly phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from 6 to 8 carbon atoms, in either a straight-chain or branched-chain configuration, with from 1 to 12 moles of ethylene oxide per mole of alkyl phenol.

Suitable nonionics also include the condensation products of aliphatic alcohols containing from 8 to 22, preferably 12 to 18, carbon atoms, in either straight-chain or branched-configuration, with from 2 to 12, preferably 3 to 7, moles of ethylene oxide per mole of alcohol.

Suitable nonionic surfactants also include the fatty acyl or alkyl condensation products of carbohydrates and their derivatives such as glycosides, aminodeoxy forms, and polyols. Examples include coco-alkyl polyglucosides and tallow-acyl polyglycerides.

The nonionic surfactants may typically be used in an amount from 0.5 to 20%, preferably from 3 to 15% and more preferably from 5 to 10%, by weight of the total detergent composition.

It should be noted that care will need to be taken in formulating an urea clathrate with certain liquid nonionics to obviate the possible replacement of acyl peroxide by the surfactant in the urea cavities.

Anionic Surfactants

The detergent compositions of the previous invention can contain, in addition to the bleaching compositions of the

present invention, one or more anionic surfactants as described below.

Alkyl Ester Sulfonate Surfactant

Alkyl ester sulfonate surfactants hereof include linear esters of C_8-C_{20} carboxylic acids (i.e. , fatty acids) which are sulfonated with gaseous SO_3 according to "The Journal of the American Oil Chemists Society", 52 (1975), pp 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry application, comprise alkyl ester sulfonate surfactants of the structural formula:

$$R^3 - CH(SO_3M) - C(=O) - OR^4$$

wherein R^3 is a C_8-C_{20} hydrocarbyl, preferably an alkyl, or combination thereof, R_4 is a C_1-C_6 hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with alkl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R^3 is C_{10}-C_{16} alkyl and R^4 is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R^3 is C_{10}-C_{16} alkyl.

Alkyl Sulfonate Surfactant

Alkyl sulfate surfactants hereof are water soluble salts or acids of the formula $ROSO_3M$ wherein R preferably is a C_{10}-C_{24} hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C_{10}-C_{20} alkyl component, more preferably a C_{12}-C_{18} alkyl or hydroxyalkyl, and M is H or a cation, e.g. an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethly-

, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethly-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Alkyl chains 12-16 carbon atoms, more preferably 14-15 carbon atoms are preferred.

Alkyl Alkoxylated Sulfate Surfactants

Alkyl alkoxylated sulfate surfactants hereof are water soluble salts or acids of the formula $RO(A)_mSO_3^M$ wherein R is an unsubstituted C_{10}-C_{24} alkyl or hydroxyalkyl group having a C_{10}-C_{24} alkyl component, preferably a C_{12}-C_{20} alkyl or hydroxyalkyl, more preferably an alkyl group having from 12 to 18 carbon atoms, especially from 12 to 15 carbon atoms.

A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like.

A preferred surfactant is C_{12}-C_{15} alkyl polyethoxylate (3.0) sulfate (C_{12}-$C_{15}E(3.0)M$). Other exemplary surfactants include C_{12}-C_{18} alkyl polyethoxylate (1.0) sulfate (C_{12}-$C_{18}E(1.0)M0$, C_{12}-C_{18} alkyl polyethoxylate (2.25) sulfate (C_{12}-$C_{18}E(2.25)M$), C_{12}-C_{18} alkyl polyethoxylate (3.0) sulfate (C_{12}-$C_{18}E(3.0)M$), and C_{12}-C_{18} alkyl polyethoxylate (4.0) sulfate (C_{12}-$C_{18}E(4.0)M$), wherein M is conveniently selected from sodium and potassium.

Other Anionic Surfactants

Other anionic surfactants useful for detersive purposes can also be included in the detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_9-C_{20} linear alkylbenzenesulphonates, C_8-C_{22} primary or secondary alkanesulphonates, C_8-C_{24} olefinsulphonates, sulphonated polycarboxylic acids prepared by sulphonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12}-C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6-C_{14} diesters), N-acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_kCH_2COO\text{-}M^+$ wherein R is a C_8-C_{22} alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation, and fatty acids esterified with isethionic acid and neutralized with sodium hydroxide. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz,

Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

Preffered anionic surfactants systems employed in the detergent compositions of the invention are free fo alkyl benzene sulfonate salts. A highly preferred system comprises a mixture of a major proportion of a C_{14}-C_{15} primary alkyl sulfate and a minor proportion of a C_{12}-C_{15} alkyl ethoxysulfate containing an average of three ethoxy groups per mole of alkyl ethoxy sulfate. The laundry detergent compositions of the present invention typically comprise from about 1% to about 20 %, preferably from about 3% to about 15% and most preferably from 5% to 10% by weight of anionic surfactants.

Other Surfactants

The detergent compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants.

Cationic detersive surfactants suitable for use in the detergent compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyldimethylanium halogenides, and those surfactants having the formula:

$$(R^2(OR^3)_y)(R^4(OR^3)_y)_2R^5N^+X^-$$

wherein R^2 is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R^3 is selected from the group consisting of $-CH_2CH_2-$, $-CH_2CH(CH_3)-$, $-CH_2CH(CH_2OH)-$, $-CH_2CH_2CH_2-$, and mixtures thereof; each R^4 is selected from the group consisting of C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, benzyl ring structures formed by joining the two R^4 groups, $-CH_2CHOH-CHOHCOR^6CHOHCH_2OH$ wherein R^6 is any hexose or hexose

polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R^5 is the same as R^4 or is an alkyl chain wherein the total number of carbon atoms of R^2 plus R^5 is not more than about 18 ; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Other cationic surfactants useful herein are also described in the U.S. Patent 4,228,044, Cambre, issued October 14, 1980, incorporated herein by reference.

When included therein, the detergent compositions of the present invention typically comprise from 0% to about 25%, preferably from about 3% to about 15% by weight of such cationic surfactants.

Ampholytic surfactants are also suitable for use in the detergent compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35 (herein incorporated by reference) for examples of ampholytic surfactants.

When included therein, the detergent compositions of the present invention typically comprise from 0% to about 15%, preferably from about 1% to about 10% by weight of such ampholytic surfactants.

Zwitterionic surfactants are also suitable for use in detergent compositions . These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S.

Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48 (herein incorporated by reference) for examples of zwitterionic surfactants.

When included therin, the detergent compositions of the present invention typically comprise from 0% to about 15%, preferably from about 1% to about 10% by weight of such zwittarionic surfactants.

Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula

$$R^3(OR^4)_xN(R^5)_2 \rightarrow O$$

wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R^5 is an alkyl or hydroxyalkyl group containing from about 1 to

about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure. These amine oxide surfactants in particular include C_{10}-C_{18} alkyl dimethyl amine oxides and C_8-C_{12} alkoxy ethyl dihydroxy ethyl amine oxides.

When included therein, the detergent compositions of the present invention typically comprise from 0% to about 15%, preferably from about 1% to about 10% by weight of such semi-polar nonionic surfactants.

Builders

The detergent compositions fo the present invention can comprise inorganic or organic detergent builders to assist in mineral hardness control. Granular formulations typically comprise at least about 1% more typically from about 10% to about 80%, preferably from about 15% to about 50% by weight of the detergent builder. Lower or higher levles of builder, however, are not meant to be excluded. Inorganic detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions (hereinafter, collectively "borate builders"), can also be used but are not preferred at wash conditions less than about 50°C, especially less than about 40°C. Prefferd builder systems are also free of phosphates.

Examples of silicate builders are the alkali metal silicates, particularly those having a SiO_2:Na_2O ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as

the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck, incorporated herein by reference. However, other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems. Examples of carbonate builders are the alkaline earth and alkali metal carbonates, including sodium carbonate and sesquicarbonate and mixtures thereof with ultra-fine calcium carbonate as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973, the disclosure of which is incorporated herein by reference.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:

$$M_z(zAlO_2 \cdot ySiO_2)$$

wherein M is sodium, potassium, ammonium or substituted ammonium, z is from about 0.5 to about 2; and y is 1; this material having a magnesium ion exchange capacity of at least about 50 milligram equivalents of $CaCO_3$ hardness per gram of anhydrous aluminosilicate. Preferred alumino-silicates are zeolite builders which have the formula:

$$Na_z[(AlO_2)_z\ (SiO_2)_y] \cdot xH_2O$$

wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al., issued October 12, 1976, incorporated herein by reference. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:

$$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot xH_2O$$

wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Specific examples of polyphosphates are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta phosphate in which the degree of polymerization ranges from about 6 to about 21, and salts of phytic acid. Examples of phosphonate builder salts are the water-soluble salts of ethane 1-hydroxy-1, 1-diphosphonate particularly the sodium and potassium salts, the water-soluble salts of methylene diphosphonic acid e.g. the trisodium and tripotassium salts and the water-soluble salts of substituted methylene diphosphonic acids, such as the trisodium and tripotassium ethylidene, isopyropylidene benzylmethylidene and halo methylidene phosphonates. Phosphonate builder salts of the aforementioned types are disclosed in U.S. Patent Nos. 3,159,581 and 3,213,030

issued December 1, 1964 and October 19, 1965, to Diehl; U.S. Patent No. 3,422,021 issued January 14, 1969, to Roy; and U.S. Patent Nos. 3,400,148 and 3,422,137 issued September 3, 1968, and January 14, 1969 to Quimby, said disclosures being incorporated herein by reference. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates. A number of ether polycarboxylates have been disclosed for use as detergent builders. Examples of useful ether polycarboxylates include oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al., U.S. Patent 3,635,830, issued January 18, 1972, both of which are incorporated herein by reference.

A specific type of ether polycarboxylates useful as builders in the present invention also include those having the general formula:

CH(A)(COOX)-CH(COOX)-O-CH(COOX)-CH(COOX)(B)

wherein A is H or OH; B is H or -O-CH(COOX)-CH_2(COOX); and X is H or a salt-forming cation. For example, if in the above general formula A and B are both H, then the compound is oxydissuccinic acid and its water-soluble salts. If A is OH and B is H, then the compound is tartrate monosuccinic acid (TMS) and its water-soluble salts. If A is H and B is -O-CH(COOX)-CH_2(COOX), then the compound is tartrate disuccinic acid (TDS) and its water-soluble salts. Mixtures of these builders are especially preferred for use herein. Particularly preferred are mixtures of TMS and TDS in a weight ratio of TMS to TDS

of from about 97:3 to about 20:80. These builders are disclosed in U.S. Patent 4,663,071, issued to Bush et al., on May 5, 1987.

Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903, all of which are incorporated herein by reference.

Other useful detergency builders include the ether hydroxypolycarboxylates represented by the structure:

$$HO-[C(R)(COOM)-C(R)(COOM)-O]_n-H$$

wherein M is hydrogen or a cation wherein the resultant salt is water-soluble, preferably an alkali metal, ammonium or substituted ammonium cation, n is from about 2 to about 15 (preferably n is from about 2 to about 10, more preferably n averages from about 2 to about 4) and each R is the same or different and selected from hydrogen, C_{1-4} alkyl or C_{1-4} substituted alkyl (preferably R is hydrogen).

Still other ether polycarboxylates include copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid.

Organic polycarboxylate builders also include the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids. Examples include the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamine tetraacetic acid, and nitrilotriacetic acid.

Also included are polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, and carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations, but can also be used in granular

compositions. Suitable salts include the metal salts such as sodium, lithium, and potassium salts, as well as ammonium and substituted ammonium salts.

Other carboxylate builders include the carboxylated carbohydrates disclosed in U.S. Patent 3,723,322, Diehl, issued March 28, 1973, incorporated herein by reference. Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986, incorporated herein by reference. Useful succinic acid builders include the C_5-C_{20} alkyl succinic acids and salts thereof.

A particularly preferred compound of this type is dodecenylsuccinic acid. Alkyl succinic acids typically are of the general formula $R\text{-}CH(COOH)CH_2(COOH)$ i.e., derivatives of succinic acid, wherein R is hydrocarbon, e.g., C_{10}-C_{20} alkyl or alkenyl, preferably C_{12}-C_{16} or wherein R may be substituted with hydroxyl, sulfo, sulfoxy or sulfone substituents, all as described in the above-mentioned patents.

The succinate builders are preferably used in the form of their water-soluble salts, including the sodium, potassium, ammonium and alkanolammonium salts.

Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Examples of useful builders also include sodium and potassium carboxymethyloxymalonate, carboxymethyloxysuccinate, cis-cyclo-hexane-hexacarboxylate, cis-cyclopentane-tetracarboxylate, water-soluble polyacrylates (these polyacrylates having molecular weights to above about 2,000 can also be

effectively utilized as dispersants), and the copolymers of maleic anhydride with vinyl methyl ether or ethylene. Other suitable polycarboxylates are the polyacetal carboxylates disclosed in U.S. Patent 4,144,226, Crutchfield et al., issued March 13, 1979, incorporated herein by reference. These polyacetal carboxylates can be prepared by bringing together, under polymerization conditions, an ester of glyoxylic acid and a polymerization initiator. The resulting polyacetal carboxylate ester is then attached to chemically stable end groups to stabilize the polyacetal carboxylate against rapid depolymerization in alkaline solution, converted to the corresponding salt, and added to a surfactant. Polycarboxylate builders are also disclosed in U.S. Patent 3,308,067, Diehl, issued March 7, 1967, incorporated herein by reference. Such materials include the water-soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, methylenemalonic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalonic acid.

Other organic builders known in the art can also be used. For example, monocarboxylic acids, and soluble salts thereof, having long chain hydrocarbyls can be utilized. These would include materials generally referred to as "soaps." Chain lengths of C_{10}-C_{20} are typically utilized. The hydrocarbyls can be saturated or unsaturated.

Enzymes

Detersive enzymes can be included in the detergent compositions of the present invention for a variety of reasons including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and prevention of refugee dye transfer. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-

activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of B.subtilis and B.licheniforms. Another suitable protease is obtained from a strain of Bacillus, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name Esperase®. The preparation of this enzyme and analogous enzymes is described in British patent specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE™ and SAVINASE™ by Novo Industries A/S (Denmark) and MAXATASE™ by International Bio-Synthetics, Inc. (The Netherlands).

Of interest in the category of proteolytic enzymes, especially for liquid detergent compositions, are enzymes referred to herein as Protease A and Protease B. Protease A and methods for its preparation are described in European Patent Application 130,756, published January 9, 1985, incorporated herein by reference. Protease B is a proteolytic enzyme which differs from Protease A in that it has a leucine substituted for tyrosine in position 217 in its amino acid sequence. Protease B is described in European Patent Application Serial No. 87303761.8, filed April 28, 1987, incorporated herein by reference. Methods for preparation of Protease B are also disclosed in European Patent Application 130,756, Bott et al., published January 9, 1985, incorporated herein by reference.

Amylases include, for example, *a*-amylases obtained from a special strain of B.licheniforms, described in more detai in British patent specification No. 1,296,839 (Novo),

previously incorporated herein by reference. Amylolytic proteins include, for example RAPIDASE™, International Bio-Synthetics, Inc. and TERMAMYL™, Novo Industries. The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4, 435, 307, Barbesgoard et al., issued March 6, 1984, incorporated herein by reference, which discloses fungal cellulase produced from Humicola insolens. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

Examples of such cellulases are cellulases produced by a strain of Humicola insolens (Humicola grisea var. thermoidea), particularly the Humicola strain DSM 1800, and cellulases produced by a fungas of Bacillus N or a cellulase 212-producing fungas belonging to the genus Aeromonas, and cellulase extracted from the hepatopancreas of a marine mollusc (Dolabella Auricula Solander).

Suitable lipase enzymes for detergent usage include those produced by micro-organisms of the of the Pseudomonas groups, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034, incorporated herein by reference. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase produced by the microorganism Pseudomonas fluorescens IAM 1057. This lipase and a method for its purification have been described in Japanese Patent Application 53-20487, laid open on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Such lipases should show a positive immunological cross-reaction with the Amano-P antibody, using the standard and well-known immunodiffusion procedure according to Ouchterlony (Acta. Med. Scan., 133, pages 76-79 (1950)). These lipases, and a method for their immunological cross-

reaction with Amano-P, are also described in U.S. Patent 4,707,291, Thom et al., issued November 17, 1987, incorporated herein by reference. Typical examples thereof are the Amano-P lipase, the lipase ex Pseudomonas fragi FERM P 1339 (available under the trade name Amano-B), lipase ex Pseudomonas nitroreducens var. lipolyticum FERM P 1338 (available under the trade name Amano-CES), lipases ex Chromobacter viscosum, e.g. Chromobacter viscosum var. lipolyticum NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further Chromobacter viscosum lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex Pseudomonas gladioli.

Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perbonate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes of pigments removed from substrates during wash operations to other substrates in the wash solution. Perodidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application Wo 89/099813, published October 19, 1989, by O.Kirk, assigned to Novo Industries A/S, incorporated herein by reference.

A wide range of enzyme materials and means for their incorporation into synthetic detergent granules is also disclosed in U.S. Patent 3,553,139, issued Jaunary 5, 1971 to McCarty et al. (incorporated herein by reference). Enzymes are further disclosed in U.S. Patent No. 4, 101, 457, Place et al., issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985, both incorporated herein by reference. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Patent

4,261,868, Hora et al., issued April 14, 1981, also incorporated herein by reference.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.5 mg to about 3 mg, of active enzyme per gram of the composition.

For granular detergents, the enzymes are preferably coated or prilled with additives inert toward the enzymes to minimize dust formation and improve storage stability. Techniques for accomplishing this are well known in the art.

Polymeric Soil Release Agent

Any polmeric soil release agents known to those skilled in the art can be employed in the detergent compositions of the present invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occuring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

Polymeric soil relese agents include cellulosic derivatives such as hydroxyether cellulosic polymers, copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polyrropylene oxide terephthalate, and the like.

Cellulosic derivatives that are functional as soil release agents are commerically available and include hydroxyethers of cellulose such as Methocel^{R} (Dow). Cellulosic soil release agents also include those selected from the group consisting of C_1-C_4 alkyl and C_4 hydroxyalkyl cellulose such as methylcellulose, ethylcellulose, hydroxypropyl methycellulose, and hydroxybutyl methylcellulose. A variety of cellulose

derivatives useful as soil release polymers are disclosed in U.S. Patent 4,000,093, issued December 28, 1976 to Nicol, et al., incorporated herein by reference.

Soil release agents characterized by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g. C_1-C_6 vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylen oxide backbones. Such materials are known in the art and are described in European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Suitable commercially available soil release agents of this kind include the Sokalan™ type of material, e.g., Sokalan™ HP-22, available from BASF (West Germany).

One type of preferred soil release agent is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. More specifically, these polymers are comprised of repeating units of ethylene terephthalate and PEO terephthalate in a mole ratio of ethylene terephthalate units to PEO terephthalate units of from about 25:75 to about 35:65, said PEO terephthalate units containing polyethylene oxide having molecular weights of from about 300 to about 2000. The molecular weight of this polymeric soil release agent is in the range of from about 25,000 to about 55,000. See U.S. Patent 3,959,230 to Hays, issued May 25, 1976, which is incorporated by reference. See also U.S. Patent 3,893,929 to Basadur issued July 8, 1975 (incorporated by reference) which discloses similar copolymers.

Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units containing 10-15% by weight of ethylene terephthalate units together with 90-80% by weight of polyoxyethlyene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300-5,000, and the mole ratio of ethylene terephthalate units to polyoxyethylene terephthalate units in the

polymeric compound is between 2:1 and 6:1. Examples of this polymer include the commercially available material Zelcon^{R} 5126 (from Dupont) and Milease ^{R} T (from ICI). These polymers and methods of their preparation are more fully described in U.S. Patent 4,702,857, issued October 27, 1987, to Gosselink, which is incorporated herein. Other suitable polymeric soil release agents include the ethyl or methyl-capped 1,2-propylene terephthalate-polyoxy- ethylene terephthalate polyesters of U.S. Patent 4,711,730, issued December 8, 1987, to Gosselink et al., the anionic end-capped oligomeric esters of U.S. Patent 4,721,580, issued January 26, 1988, to Gosselink, wherein the anionic end-caps comprise sulfo-polyethoxy groups derived from polyethylene glycol (PEG), the block polyester oligomeric compounds of U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink, having polyethoxy end-caps of the formula $X-(OCH_2CH_2)_n-$ wherein n is from 12 to about 43 and X is a C_1-C_4 alkyl, or preferably methyl, all of these patents being incorporated herein by reference.

Additional soil release polymers include soil release polymers of U.S. Patent 4,877,896, issued October 31, 1989 to Maldonado et al., which discloses anionic, especially sulfoaroyl, end-capped terephthalate esters, said patent being incorporated herein by reference. The terephthalate esters contain unsymmetrically substituted oxy-1,2-alkyleneoxy units.

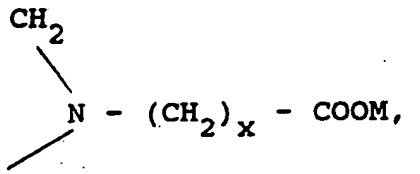
If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent composi-tions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%. October 31, 1989 to Maldonado et al. All of these patents are incorporated herein by reference.

If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent composi-tions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

Chelating Agents

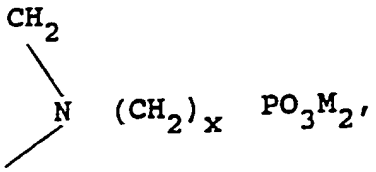
The detergent compositions of the present invention may also contain one or more iron and manganese chelating agents as a builder adjunct material. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents in compositions of the invention can have one or more, preferably at least two, units of the substructure

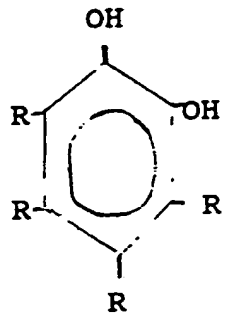


wherein M is hydrogen, alkali metal, ammonium or substituted ammonium (e.g. ethanolamine) and x is from 1 to about 3, pref- erably 1. Preferably, these amino carboxylates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms. Operable amine carboxylates include ethylenediaminetetraacetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetraproprionates, triethylenetetraaminehexa-acetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts thereof and mixtures thereof.

Amino phosphonates are also suitable for use as chelating agents in the detergent compositions of the invention when at least low levels of total phosphorus are permitted in detergent composi- tions. Compounds with one or more, preferably at least two, units of the substructure



wherein M is hydrogen, alkali metal, ammonium or substituted ammonium and x is from 1 to about 3, preferably 1, are useful and include ethylenediaminetetrakis (methylenephosphonates), nitrilotris (methylenephosphonates) and diethylenetriaminepentakis (methylenephosphonates). Preferably, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms. Alkylene groups can be shared by substructures. Polyfunctionally - substituted aromatic chelating agents are also useful in the compositions herein. These materials can comprise compounds having the general formula:



wherein at least one R is $-SO_3H$ or -COOH or soluble salts thereof and mixtures thereof. U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al., incorporated herein by reference, discloses polyfunctionally - substituted aromatic chelating and sequestering agents. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy -3,5-disulfo- benzene. Alkaline detergent compositions can contain these materials in the form of alkali metal,

ammonium or substituted ammonium (e.g. mono-or triethanol-amine) salts.

If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent composi-tions herein. More preferably chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Clay Soil Removal/Anti-redeposition Agents

Clay soil removal/anti-redeposition agents useful in the detergent compositions of the present invention include polyethylene glycols and water-soluble ethoxylated amines having clay soil removal and anti-redeposition properties, as well as additional polyamino compounds derived from aspartic acid but not containing glutamic acid.

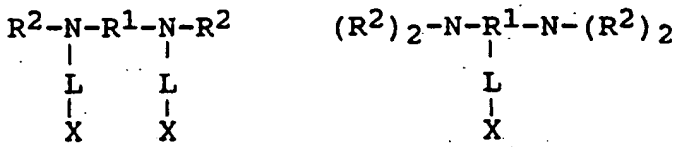
Polyethylene glycol compounds useful in the detergent compositions of the present invention typically have a molecular weight in the range of from to about 1,000 to about 20,000, more preferably from about 2,000 to about 12,000, most preferably from about 4,000 to about 8,000. Such compunds are commercially available and are sold as Carbowax®, which is available from Union Carbide, located in Danbury, Conn.

The water soluble ethoxylated amines are preferably selected from the group consisting of :

(1) ethoxylated monamines having the formula :

$$(X\text{-}L)\text{-}N\_R(R^2)_2$$

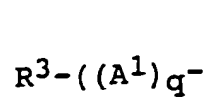
(2) ethoxylated diamines having the formula :



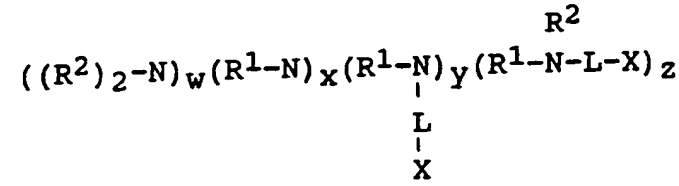
or

$$(X\text{-}L)_2\text{-}N\text{-}R^1\text{-}N\text{-}(R^2)_2$$

(3) ethoxylated polyamines having the formula :

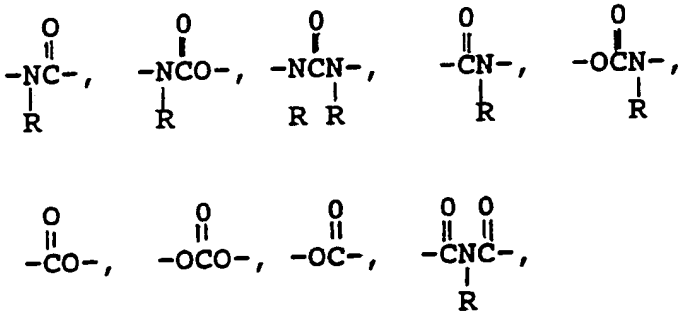


(4) ethoxylated amine polymers having the general formula :



and

(5) mixtures thereof; wherein A^1 is :



or -O-; R is H or C_1-C_4 alkyl or hydroxyalkyl R^1 is C_2-C_{12} alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C_2-C_3 oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-N bonds are formed ; each R^2 is C_1-C_4 or hydroxyalkyl, the moiety -L-X, or two R^2 together form the moiety $-(CH_2)_r$, $-A^2-(CH_2)_s-$, wherein A^2 is -O- or $-CH_2-$, r is 1 or 2, s is 1 or 2, and r + s is 3 or 4 ; X is a nonionic group, an anionic group or mixture thereof ; R^3 is a substituted C_3-C_{12} alkyl, hydroxyalkyl, alkenyl, aryl, or alkaryl group having substitution sites ; R^4 is C_1-C_{12} alkylene, hydroxyakylene, alkenylene, arylene or alkarylene, or a C_2-C_3 oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-O or O-N bonds are formed ; L is a hydrophilic chain which contains the polyoxyalkylene moiety $-((R^5O)_m(CH_2CH_2O)_n)-$, wherin R^5 is C_3-C_4 alkylene or hydroxyalkylene and m and n are numbers such that the moiety $-CH_2CH_2O)_n-$ comprises at least about

50% by weight of said polyoxyalkylene moiety ; for said monamines, m is from 0 to about 3, and n is at least about 6 when R^1 is C_2-C_3 alkylene, hydroxyalkylene, or alkenylene, and at least about 3 when R^1 is other than C_2-C_3 alkylene, hydroyalkylene or alkenylene ; for said polyamines and amine polymers, m is from 0 to about 10 and n is at least about 3 ; p is from 3 to 8 ; q is 1 or 0 ; t is 1 or 0, provided that t is 1 when q is 1 ; w is 1 or 0 ; x + y + z at least 2 ; and y + z is at least 2.

The most preferred soil release and anti-redeposition agent are ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued July 1, 1986, incorporated herein by reference. Another group of preferred clay soil removal/anti-redeposition agents are the cationic compounds disclosed in European Patent Application 111,965, Oh and Gosselink, published June 27, 1984, incorporated herein by reference. Other clay soil removal/anti-redeposition agents which can be used include the ethoxylated amine polymers disclosed in European Patent Application 111,984, Gosselink, published June 27, 1984; the zwitterionic polymers disclosed in European Patent Application 112,592, Gosselink, published July 4, 1984; and the amine oxides disclosed in U.S. Patent 4,548,744, Connor, issued October 22, 1985, all of which are incorporated herein by reference.

The most preferred soil release and anti-deposition agents are ethoxylated tetraethylenepentamine and the polythylene glycols having a molecular weight in the range of from about 4,000 to about 8,000.

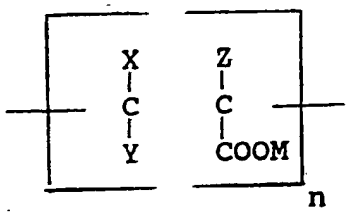
Granular detergent compositions which contain such compounds typically contain from about 0.01% to about 10.0% by weight of the clay removal agent.

Polymeric Dispersing Agent

Polymeric polycarboxylate dispersing agents can advantageously be utilized in the detergent compositions

of the present invention. These materials can aid in calcium and magnesium hardness control. In addition to acting as a builder adjunt analogously to the poycarboxylate described above in the Builder description, it is believed, though it is not intended to be limited by theory, that these higher molecular weight dispersing agents can further enhance overall detergnet builder performance by inhibiting crystal growth of inorganics, by particulate soil peptization, and by antiredeposition, when used in combination with other builders including lower molecular weight polycarboxylates.

The polycarboxylate materials which can be employed as the polymeric polycarboxylate dispersing agent are these polymers or copolymers which contain at least about 60% by weight of segments with the general formula :



wherein X, Y, and Z are each selected from the group consisting fo hydrogen, methyl, carboxy, carboxmethyl, hydroxy and hydroxymethyl; a salt forming cationand n is from about 30 to about 400. Preferably, X si hydrogen or hydroxy, Y is hydrogent or carboxy, Z is hydrogen and M is hydrogen, alkali metal, ammonia or substituted ammonium. Polymeric polycarboxylate materials of this type can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polymeric polycarboxylates herein of monomeric segments, containing no carboxylate radicals such as vinylmethyl

ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions have been disclosed, for example, in Diehl, U.S. Patent No. 3,308,067, issued March 7, 1967. This patent is incorporated herein by reference.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing agent. Such materials include the water soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form ranges from about 5,000 to 100,000, preferably from about 6,000 to 60,000, more preferably from about 7,000 to 60,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, moe preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are knwon materials which are described in European Patent Application No. 66915, published December 15, 1982, which publication is incorporated herein by reference.

Polyamino dispersant compounds derived from aspartic acid but not containing glutamic acid are useful as additional polyamino disperant compounds in the detergent

compositions of the invention. Such polyamino dispersant compounds suitable for inclusion herein are disclosed in EP-A--305282, EP-A-305283 and EP-A-351629.

If utilized, the polymeric dispersing agents will generally comprise from about 0.2% to about 10%, preferably form about 1% to about 5% by weight of the laundry detergent compositions.

Brightener

Optical brighteners or other brightening or whitening agents known to those skilled in the art can be incorporated into the laundry detergent compositions of the present invention. However, the choice of brightener will depend upon a number of factors, such as the type of detergnt, the nature of other components present in the detergent composition, the temperatures of wahs wash, the degree of agitation, and the ratio of the material washed to tub size.

The brightener selection is also dependent upon the type of material to be cleaned, e.g. cottons, synthetics, etc. Since most laundry detergent products are used to clean a variety of fabrics, the detergent compositions should contain a mixture of brighteners which will be effective for a variety of fabrics. It is of course necessary that the individual components of such a brightener mixture be compatible.

Commercial optical brighteners can be classified into subgroups which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiphene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982), the disclosure of which is incorporated herein by reference.

Stilbene derivatives include, but are not necessarily limited to, derivatives of stilbene; triazole derivatives

of stilbene; oxadiazole derivatives of stilbene; oxazole derivatives fo stilbene; and stryl of stilbene.

Certain derivatives of bis(triazinly) aminostilbene may be prepared from 4,4'-diamine-stilbene-2,2'-disulfonic acid.

Coumarin derivatives include, but are not necessarily limited to, derivatives substituted in the 3-position, in the 7-position, and in the 3- and 7-positions.

Carboxylic acid derivatives include, but are not necessarily limited to, fumaric acid derivatives; benzoic acid derivatives; p-phenylene-bis-acrylic acid derivatives; naphthalenedicarboxylic acid derivatives; heterocyclic acid derivatives; and cinnamic acid derivatives.

Cinnamic acid derivatives can be further subclassified into groups which include, but are not necessarily limited to, cinnamic acid derivatives, styrylazoles, styrylbenzofurans, styryloxadiazoles, styryltriazoles, and styrylpolyphenyls, as disclosed on page 77 of the Zahradnik reference.

The styrylazoles can be further subclassified into styrylbenzoxazoles, styrylimidazoles and styrylthiazoles, as disclosed on page 78 of the Zahradnik reference. It will be understood that these three identified subclasses may not necessarily reflect an exhaustive list of subgroups into which styrylazoles may be subclassified.

Other optical brighteners are the derivatives of dibenzothiophene-5,5-dioxide disclosed at page 741-749 of The Kirk-Othmer Encyclopedia of Chemical Technology, Volume 3, pages 737-750 (John Wiley & Son, Inc., 1962), the disclosure of which is incorporated herein by reference, and include 3,7-daiminodibenzothiophene-2, 8-disulfonic acid5, 5 dioxide.

Other optical brighteners are azoles, which are derivatives of 6-membered ring heterocycles. These can be further subcategorized into monoazoles and bisazoles. Examples of monazoles and bisazoles are disclosed in the Kirk-Othmer reference.

Examples of such compounds include brighteners derived from pyrazine and brighteners derived from 4-aminonaphthalamide.

In addition to the brighteners already described, miscellaneous agents may also be useful as brighteners. Examples of such miscellaneous agents are disclosed at pages 93-95 of the Zahradnik reference, and include 1-hydroxy-3,6,8-pyrenetrisulfonic acid; 2,4-dimethoxy-1,3,5-triazin-6-yl-pyrene; 4,5-diphenylimidazolonedisulfonic acid; and derivatives of pyrazolinequinoline.

Other specific examples of optical brightener are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13,1988, the disclosure of which is incorporated herein by reference. Thse brighteners include the Phorwhite™ series of brighteners from Verona. Others brighteners disclosed in this reference include : Tinopal UNPA, Tinopal CBS adn Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, available from Hilton-Davis, located in Italy; the 2-(4-styrylphenyl)-2H-naphthol(1,2-d)triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbene; 4,4'-bis(styryl)bisphenyls; and the y-amino-coumarins. Specific examples of these brighteners include 4-methyl-7-diethylamino coumarin; 1,2-bis(-bensimidazol-2-yl)-ethylene; 1,3-diphenylphrazolines; 2,5-bis(benzoxazol-2-yl)-thiophene; 2-styryl-naphth-(1,2-d)-oxazole; and 2-(stilbene-4-yl)-2H-naphtho(1,2-d)triazole.

Still other optical brighteners include those disclosed in U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton, the disclosure of which is incorporated herein by reference.

If utilized, the optical brighteners will generally comprise from about 0.05% to about 2.0%, preferably from about 0.1% to about !.0% by weight of the laundry detergent compositions.

Suds Suppressors

Compounds known, or which become known, for reducing or suppressing the formation of suds can be incorporated into the detergent compositions of the present invention. The incorporation of such materials , hereafter "suds supressor", can be desirable because the polyhydroxy fatty

acid amide surfactants hereof can increase suds stability of the detergent compositions. Suds suppression can be of particular importance when the detergent compositons include a relatively high sudsing surfactant in combination with the polyhydroxy fatty acid amide surfactant.

Suds suppression is particularly desirable for compositions intended for use in front loading automatic washing machines. These machines are typically characterized by having drums, for containing the laundry and wash water, which have a horizontal axis and rotary action about the axis. This type of agitation can result in high suds formation and, consquently, in reduced cleaning performance. The use of suds suppressors cna also be of particular importance under hot water wahsing conditions and under high surfactant concentration conditions.

A wide variety of materials may be used as suds suppressors. Suds suppressors are well known to those skilled in the art. They are generally described, for example, in Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One categroy of suds suppressor of particular interest encompasses monocarboxylic fatty acids and soluble salts thereof. These materials are discussed in U.S. Patent 2,954,347, issued September 27, 1960 to Wayne St. John, said patent being incorporated herein by reference. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressors typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts. These materials are a preferred category of suds suppressor for detergent compositions.

The detergent compositions of the present invention may also contain non-surfactant suds suppressors. These include, for example, high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid

triglycerides), fatty acid esters of monovalent alcohols, aliphatic C_{18}-C_{40} ketones (e.g. stearone), etc. Other suds inhititors include N-alkylated amino triazines such as tri- to hexa-alkylemlamines or di- to tetra-alkyldaimine chlortriazines formed as products of cyanuric choloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., sodium, potassium, lithium) phosphates and phosphate esters. The hydrocarbons, such as paraffin and haloparaffin, can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of about -40°C and about 5°C, and a minimum boiling point not less than about 100°C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below about 100°C. The hydrocarbons constitute a preferred category of suds suppressor for detergent compositions. Hydrocarbon suds suppressors are described for example in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al., incorporated herein by reference. The hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from about 12 to about 70 carbon atoms. The term "parrafin", as used in this suds suppressor discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

Another preferred category of non-surfactant suds comprises silicone suds suppressors. This category includes the use fo polyorganosiloxane oils, such as polydimethysiloxane, dispersions or emulsions fo polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed of fused onto the silica. Silicone suds suppressors are well known in the art and are, for example disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al.,

and European Patent Application No. 89307851.9, published February 7, 1990, by Starch, M.S., both incorporated herein by reference.

Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839, which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672, Bartolotta et al., and in U.S. Patent 4,652,392, Baginski et al., issued March 24, 1987.

An exemplary silicone based suds suppressor for use herein is a suds suppressing amount of a suds controlling agent consisting essentially of :

(i) Polydimethlsiloxane fluid having a viscosity of from about 20 cs. to about 1500 cs. at 25°C;

(ii) From about 5 to about 50 parts per 100 parts by weight of :

(i) of siloxane resin composed of $(CH_3)_3$ $SiO_{1/2}$ units of S_iO_2 units in a ratio of from $CH_3)_3SiO_{1/2}$ units and to SiO_2 units of from about 0.6:1 to about 1.2:1; and

(iii) from about 1 to about 20 parts per 100 parts by weight of :

(i) of a solid silica gel :

Suds suppressors, when utilized, are present in a "suds suppressing amoung". By "suds suppressing amount" is meant that he formulator of the composition can select an amount of this suds controlling agent that will control the suds to the extent desired. Teh amount of suds control will vary with the detergent surfactant selected. Fro example,

with high sudsing surfactants, relatively more of the suds controlling agent is used to achieve the desired suds control than with low foaming surfactants.

The detergent compositions of the present invention will generally comprise from 0% to about 5% of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts thereof, will be present typically in amounts up to about 5%, by weight, of the detergent composition. Preferably, from about 0.5% to about 3% of fatty monocarboxylate suds suppressor is utilized. Silicone suds suppressors are typically utilized in amounts up to about 2.0%, by weight, of the detergent composition, although higher amounts may be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling sudsing. Preferably from about 0.01% to about 1% of silicone suds suppressor is used, more preferably from about 0.25% to about 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any adjunct materials that may be utilized. Monostearyl phosphates are generally utilized in amounts ranging from about 0.1% to about 2% by weight of the compositions. Hydrocarbon suds suppressors are typically utilized in amounts ranging from about 0.01% to about 5.0%, although higher levels can be used.

Bleach activators

The detergent compositions of the present invention may contain one or more bleach activators.

If present, the amountof bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40%, of the bleaching composition (i.e. the total of bleaching active plus bleach activator).

A wide range of bleach activators can be used, examples being disclosed in Spadini et al USP 4179390. Preferred bleach activators include tetraacetyl alkylene diamines,

particularly tetraacetyl ethylene diamine (TAED) and tetraacetyl (TAGU). Other activators that come into consideration are the compounds of the formula :

R - CO - L

10.5. Techniques for controlling pH at recommended usuage levels include the use of buffers, alkalis, acids, etc and wherein R is an alkyl group containing from about 1 to 18 carbon atoms wherein the longest linear alkyl chain extending from and including the carbonyl carbon contains from about 6 to about 10 carbon atoms and L is a leaving group, the conjugate acid of which has a pK_a in the range of from 4 to about 13. These bleach activators are described in U.S. Patent 4,915,854, issued April 10, 1990 to Mao, et al., incorporated herein by reference, and U.S. Patent 4,412,934, which was previously incorporated herein by reference. Nonanoyloxybenzene sulfonate (NOBS) is another preferred bleach activator.

The compositions of this invention may be formulated so that during aqueous cleaning operations the wash water will have a pH of, for example, 6.5 to 11, typically 7.5 to 10.5. Techniques for controlling pH at recommended usuage levels include the use of buffers, alkalis, acids, etc and are well known in the art.

In use, the composition of the present invention will be dissolved in an aqueous medium, typically tap water, ad the fabric to be cleaned will be immersed in the resultant bleaching or washing liquor, with agitation if appropriate. The compositions can be used for soaking, for washing by hand or in automatic laundry washing machines. The concentration of actives in the said liquor, the temperature, the degree of agitation and the duration of the immersion may be varied, depending upon the nature of the fabric and the amount of soiling.

Granular bleaching compositions and granular detergent compositions, to be effective and acceptable, must be readily dispersible in aqueous media. In the article by

L. Heslinga and W. Schwaiger, Recueil, 85 (1966), 75 at page 85, it is stated that caprylyl peroxide (i.e. dioctanoyl peroxide) is sparingly soluble in an aqueous perbonate solution (pH 10) at room temperature and that the perhydrolysis under these conditions is negligible. Surprisingly, however, it has been found by the present applicant that, when employed in the form of their urea clathrates in accordance with this invention, the peroxides have a very acceptable dispersability in aqueous media and give excellent bleaching performance. This may be manifest in various ways : thus, for example, certain embodients are very effective against carotenoid stains that have proved resistant to bleaching systems of the prior art, whereas certain other embodiments are comparable to or better than conventional bleaching systems even in the absence of perbonate.

Granular bleaching compositions and bleach containing granular detergent compositions should also possess good bleach storage stability. The urea clathrates diacyl and tetraacyl peroxides in accord with this invention demonstrate good storage stability, even in the alkaline conditions of a detergent composition.

The present compositions have certain advantages over the compositions disclosed in EP-A-0, 106, 584, which form diacyl peroxide *in situ*, in that the level of diacyl peroxide can be more accurately determined; moreover, the present invention permits the benefits of diacyl peroxide bleaching to be obtained even in situations where the use of NOBS and/or perbonate is contraindicated.

A further unexpected advantage of the present invention is that, although the presence of a bleach activator is not precluded, certain compositions according to the present invention can give excellent results in the absence of the activator. Conventionally, the bleach activator (e.g. NOBS or TAED) has been included in perbonate-containing compositions in order to produce a peroxy acid *in situ*, such acids being effective in the bleaching of non-carotenoid

hydrophobic stains (as in the case of peroxynonanoic acid produced by NOBS) or hydrophilic stains (as in the case of peroxyacetic acid produced by TAED). However, and whilst not wishing to be bound by any theory, it is believed that the diacyl or tetraacyl peroxide and the perbonate (or other H_2O_2 source) present in the compositions will give rise to a reaction in the aqueous medium to form peroxy acid, thereby providing a system benefitting from the bleaching properties of both the diacyl or tetraacyl peroxide and the peroxy acid, even in the absence of a conventional bleach activator. For instance, the compound of the formula :

$$C_9H_{19}\text{-NHCO-}(CH_2)_4\text{-CO-OO-CO-}CH_3$$

is believed to react with perbonate *in situ* to produce two effective bleaching agents, namely :

C_9H_{19}-NHCO-$(CH_2)_4$-C(=O)OOH (NAAPA0 and

$CH_3C(=O)OOH$ (peroxyacetic acid).

The present invention is illustrated in and by the following examples :

Example 1

Dinonanoyl peroxide was prepared, using the method of L.S. Silbert and D. Swern, J. Amer. Chem. Soc. 81 (1959) 2364, as follows. Nonanoyl chloride, 17.6g, was dissolved in diethyl ether (176 ml) and the solution was cooled to 0°C. 60% aqueous hydrogen peroxide (4.25 ml) was added dropwise followed by pypridine (9.5 g), also added dropwise, with vigorous stirring and maintenance of the temperature between 0 and 5°C by means of an ice-bath. The ice-bath was then removed and stirring was continued for 1 hour. Diethyl ether was added to dilute the reaction mixture which was then washed with dilute HC1, 5% $KHCO_3$, and finally water. After drying (Na_2SO_4), filtration and rotary evaporation, a product, of melting point 13°C, was islolated, which product analysed as 86.5% diacyl peroxide.

The urea clathrate of dinonanoyl peroxide was prepared as follows. Dinonanoyl peroxide (10 g) was dissolved in the minimum volume of warm (40°C0 methanol. Urea (50 g) was dissolved in hot methanol (200 ml) and the solutions were mixed and then cooled to yield an immediate precipitate of clathrate. Filtration and drying produced a product (31 g) analysed as containing 29% diacyl peroxide.

Example 2

Dioctanoyl peroxide, obtained as the commercial product Perkadox SE8 from Akzo, was reacted with urea in the manner described above in Example 1 to yield an urea clathrate analyses as containing 27.5% diacyl peroxide.

Example 3

Diacetyl azelaic diperoxide was prepared as follows. Diperoxy azelaic acid (prepared by the method of Parker *et al*, J. Amer. Chem. Soc., 79 (1957) 1929) in an amount of 50 g was dissolved in acetic acid (500 ml) in an open beaker (magnetic stirrer) and cooled to below 20°C. Pyridine (38 g) was added dropwise over a period of 15 min, with extra cooling to maintain the temperature below 20°C. The white suspension was thus converted to a clear solution; reaction was continued for a further 30 min at room temperature. The solution was poured onto ice-water (20 1) with vigorous stirring whereupon a white solid separated, which was filtered, washed and dried, 51 g, m.pt. 53°C (literature value, 51-53°C). Analysis indicated freedom from peracid and a tetraacyl peroxide content of 92%.

To form the clathrate, diacetyl azelaic diperoxide (40 g) was dissolved in the minimum volume of warm (40°) methanol and was mixed with a hot solution of urea (120 g) in methanol (1 litre). On cooling, a heavy white precipitate of clathrate formed, which was filtered and dried, 130 g. Analysis indicated a tetraacyl peroxide activity of 27.8%.

Example 4

Laundry detergent compositions according to this invention may be prepared by adding the urea clathrate of dinonanoyl

peroxide, the urea clathrate of dioctanoyl peroxide or the urea clathrate of diacetyl azelaic diperoxide to either of the following base formulations (the amounts being in parts by weight).

Table 1

Component	A	B
LAS	7.5	7.8
TAS	2.5	2.4
45E7	4.0	4.0
TAE11	1.35	-
Silicate	3.0	2.7
MA/AA	2.0	1.0
Polyacylate	-	5.6
DETPMP	0.3	0.6
CMC	0.48	0.48
Zeolite	23.6	23.0
Silicone Prill	2.75	2.75

The components are as follows :

LAS = sodium linear C_{12}-alkyl benezene sulfonate.

TAS = sodium tallow alcohol sulfonate.

45E7 = synthetic C_{14}/C_{15} alcohol ethoxylated with 7 moles of ethylene oxide per mole of alcohol.

TAE11 = tallow alcohol ethoxylated with 11 moles of ethylene oxide per mole of alcohol.

Silicate = sodium silicate having an $SiO_2:Na_2O$ ratio of 1.6.

MA/AA = copolymer of 1:4 maleic and acrylic acids average molecular weight of about 80,000.

Polyacrylate = homopolymer of acrylic acid, molecular weight of 4000.

DETPMP = diethylene triamine penta(methylene phosphonic acid) marketed by Monsanto under the trade name "Dequest 2060".

CMC = sodium carboxymethylcellulose.

Zeolite = hydrated sodium aluminosilicate of formula $Na_{12}(AlO_2.SiO_2)_{12}.27H_2O$ and

having a primary particle size of 1-10um.

Silicone Prill = 0.14 parts by weight of an 85:15 mixture (by weight) silanated silica and silicone, granulated with 1.3 parts of sodium tripolyphosphate, and 0.56 parts of tallow alcohol condensed with 80 molar proportions of ethylene oxide.

The urea clathrates may be added in an amount, for example, equivalent to 1% by weight acyl peroxide or 1.5% by weight acyl peroxide, relative to the base formulation. Sodium perbonate monohydrate may also be added to provide a content thereof in the compositions of, for example, 16% by weight.

Example 5

In order to test the effectiveness on carotenoid-type stains, two test laundry detergent compositions were prepared by adding the urea clathrate of dinonanoyl peroxide (the clathrate containing 30% active compound) in amounts of 1 percent by weight and 1.5% percent by weight, respectively, to a perbonate-containing (16% by weight perbonate monohydrate) granular detergent composition, hereinafter referred to as the "base" composition. Stained fabrics were washed at 30°C in a commercially available domestic washing machine using the above described formulations, and the stain removal was judged by an expert panel in known manner, the results being recorded in panel score units (psu) on the Scheffé scale, taking the results obtained using the base composition (no added diacyl peroxide clathrate) as the standard. The results are given in the following table :

Table 2

Stain	Base	Base + 1.5% clathrate	Base + 1.0% clathrate
Carrot baby food	0.00	+ 3.50	+ 3.38
Spaghetti sauce	0.00	+ 2.88	+ 2.44

Tomato purée	0.00	+ 2.50	+ 2.25
Carrot/tomato, dried	0.00	+ 1.13	+ 1.94

The above results show that the addition of the dinonanoyl peroxide/urea clathrate, at either of the stated levels of addition, gave rise to a significant improvement in respect of the cleaning of the above-identified stains.

Example 6

The effectiveness of dioctanoyl peroxide (DOP) and of diacetyl azelaic diperoxide (DAAP), in both cases in the form of the urea clathrate, was tested against certain hydrophilic (specifically, tea/wine), hydrophobic (specifically, paprika) and carotenoid (specifically, tomato) stains. For comparison purposes, tests against the stains were also carried out using isononanoyloxybenzene sulfonate (i-NOBS), tetraacetylethylenediamine (TAED) and the compound of the formula C_9H_{19} - NHCO-(CH_2)-CO-OOH (NAPAA).

The test compositions were prepared by adding the DOP, DAAP, i-NOBS, TAED and NAPAA to respective samples f a base formulation similar to that disclosed in Example 4B above, at a level of 5% by weight relative to said base formulation. Sodium perbonate was also included in certain of the test compositions.

The tests were carried out under standard conditions (SPIT Launderometer, 18°H water, 40°C and equal weight bleaches). For the hydrophilic stains, bleaching effectiveness was evaluated in terms of the reflectance parameter L in the Hunter "L, a, b" tristimulus system using a Hunterlab Colormeter: the differences ΔL with respect to the standard are a sufficient indication of "whiteness" differences. For the other stains, panel judging was employed, as described in Example 5. The results, relative to i-NOBS taken as the standard, are given in the Table which follows :

Table 3

	Hydrophilic(ΔL)	Hydrophobic (psu)	Carotenoid (psu)
i-NOBS	0	0	0
TAED	+ 2.9	- 2.5	- 4.0
NAPAA	- 2.0	+ 0.8	- 1.5
DOP	+ 2.6	+ 1.3 (+0.8)	+ 3.0 (+4.0)
DAAP	+ 3.0	- 2.5 (-0.4)	- 4.0 (-0.9)

The results shown in parenthesis were obtained in the absence of perbonate; all other tests were carried out using the same level of perbonate. The results show that dioctanoyl peroxide/urea clathrate gave excellent results against the hydrophobic and, especially the carotenoid stains whilst its effectiveness against the hydrophilic stain was comparable to that obtained using the known activator TAED.

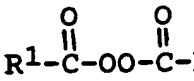
The results of DAAP in the presence of perbonate are comparable to those for TAED, which is currently regarded as a potent ingredient of conventional detergent compositions. In the absence of perbonate, however, DAAP gave a score 3.1 psu higher than that given by TAED on carotenoids, which represents a significant improvement in performance.

It will of course be understood that the present invention has been described above purely by way of example and that modifications of detail can be made within the scope of the invention.

CLAIMS

1. A bleaching composition comprising :

(A) an urea clathrate of a peroxide compound, the peroxide compound being selected from the group consisting of (1) diacyl peroxides of the general formula :



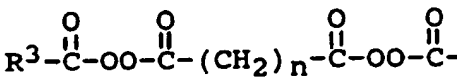
(1)

in which :

R^1 represents a C_6-C_{18} alkyl group containing a linear chain of at least 5 carbon atoms and optionally containing one or more substituents and/or one or more interrupting moieties interpolated between adjacent carbon atoms of the alkyl radical and

R^2 represents an apilphatic or aromatic group compatible with a peroxide moiety, such that R^1 and R^2 together contain a total of 8 to 30 carbon atoms,

and (2) tetraacyl peroxides of the general formula :



(2)

in which

R^3 represents a C_1-C_9 alkyl group, and n represents an integer from 2 to 12 inclusive.

2. A composition according to Claim 1 that comprises an urea clathrate of a diacyl peroxide of the formula (1) in which R^1 and R^2 each represent an unsubstituted and uninterrupted alkyl group.

3. A composition according to claim 2, that comprises a urea clathrate of a diacyl peroxide of the formula (1) in which R^1 and R^2 each represent an unsubstituted and uninterrupted alkyl group.

4. A composition according to claim 2 or 3, that comprises an urea clathrate of a diacyl peroxide of the formula (1) in which R^1 and R^2 represent identical straight-chain alkyl groups.
5. A composition according to claim 1, that comprises an urea clathrate of a tetraacyl peroxide of the formula (2) in which n represent an integer from 4 to 10.
6. A composition according to claim 1 that comprises an urea clathrate of a peroxide of the formula :

$$n\text{-}H_{17}C_8\text{-}CO\text{-}OO\text{-}CO\text{-}C_8H^{17}\text{-}n,$$

$$n\text{-}H_{15}C_7\text{-}CO\text{-}OO\text{-}CO\text{-}C_7H_{15}\text{-}n,$$

$$H_3C\text{-}CO\text{-}OO\text{-}CO\text{-}(CH_2)_7\text{-}CO\text{-}OO\text{-}CO\text{-}CH_3$$

or $$H_3C\text{-}CO\text{-}OO\text{-}CO\text{-}(CH_2)_{10}\text{-}CO\text{-}OO\text{-}CO\text{-}CH_3$$

7. A bleaching detergent composition according to any of Claims 1 to 6 incorporating :
(B) a source of hydrogen peroxide.
8. A detergent composition comprising the bleaching composition according to any of Claims 1 to 7, wherein said detergent composition comprises :
(C) detersive surfactant.
9. A composition according to any of claims 1 to 8 that comprises an amount of urea clathrate (A) corresponding to a level of 0.1 to 20 percent by weight of acyl proxide, relative to the total composition.
10. A composition according to any of Claims 7 to 9, in which the component (B0 is a percarbonate or a perborate.
11. A composition according to any of Claims 7 to 10, that comprises the component (B) in an amount of from 0.5 to 60 percent by weight, relative to the total composition.

12. A composition according to any of Claims 8 to 11, comprising a detersive surfactant (C), which composition also comprises (D) a detergency building compound.
13. A composition according to any of Claims 1 to 12, that also comprises (E) a bleach activator.
14. The use, as a bleaching agent, of an urea clathrate of a peroxide of the formula (1) or (2) as defined in any of Claims 1 to 6.

INTERNATIONAL SEARCH REPORT

[redacted] S92/08301

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C01B 15/00
US CL :252/186.23, 186.26, 186.27, 95
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. :

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	N, CA 114(26): 257275Q (Harris et al.) Dept. Phys. Chem. Univ. Cambridge, UK. 1990 "Structural Properties of...dirc l peroxite in urea inclusion compounds."	1-4,6,9 5,7-8.10-14
X Y	N, CA 114(2): 15267P (Harris et al.) Dept. Phys. Chem. Univ. Cambridge, UK 1990 "Structural aspects of urea inclusion compounds..."	1-4,6,9 5,7-8,10-14
X Y	N, CA 110(11): 943905 (Casai et al.) Div. Chem., Natl. Res. Counc. Canada, 1989, "Behavior or Alkyl Radical Pairs in Urea Channels Photolysis of ... Urea/di cyl peroxide complexes."	1-4,6,9 5,7-8,10-14

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

12 NOVEMBER 1992

Date of mailing of the international search report

06 JAN 1993

Name and mailing address of the ISA/
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Washington, D.C. 20231

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Authorized officer

JOSEPH D. ANTHONY

Telephone No. (703) 308-0446

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/08301

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,529,534 (Richardson) 16 July 1985, (See example 1).	1-14
A	US, A, 4,560,495 (Kato) 24 December 1985, (See abstract, claims).	1-14
A	US, A, 4,087,369 (Wevers) 02 May 1978, (See abstract).	1-14

INTERNATIONAL SEARCH REPORT

International application No.
P[redacted]92/08301

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

CA Search
urea#
clathrate#
inclusion?
complex? adduct?